

## DECLARATION

I, Karl Siemensmeyer, state that I am a resident of 67227 Frankenthal, Erich-Heckel-Strasse 1, Federal Republic of Germany; that I am a citizen of the Federal Republic of Germany; that I am a chemist having graduated at the University of Paderborn, Paderborn, Federal Republic of Germany;

that I was employed as a scientific staff member with the University of Paderborn from 1985 to 1989,

that I entered BASF Aktiengesellschaft in 1989, where I have been working (worked) in the fields of liquid crystal research from 1989 to 1996, of marketing and development of textile ink-yet printing from 1997 to 2001 and since then in the field of marketing and development of textile dyeing auxiliaries;

that I am acquainted with the subject matter of U.S. Patent Application Serial No. 09/644,220, filed August 23, 2000, by Reinhard Schneider, Peter Maier, Eberhard Beckmann and Ulrich Karl for "Lightening dyed textile material";

that I consider myself qualified by my knowledge of chemistry and especially of structure, composition and application of textile dyeing auxiliaries and by my seven years' experience in this field;

that I have read U.S. Patent No. 4,227,881 to Fono and the International Patent Publication WO 98/03725 to Beckmann as well as the Office Actions of 07/31/2002 (paper no. 4), 02/14/2003 (paper no. 7) and the Advisory Action of 07/11/2003 and wish to make the following observations (Numbers in square brackets refer to attached list of cited literature):

The present invention is concerned with a process for partial lightening textile materials, particularly denim material which is to be used for the production of „blue jeans“.

An essential feature of this process is, that it does not destroy or reduce the characteristic look of the Denim fabric which results from weaving colored warp- and uncolored weft-threads.

In the process of the present invention a lightening liquid is used consisting of an aqueous solution of an aminoalkane sulfinat, optionally together with an aminoalkane sulfonate.

Additional auxiliary agents can be used and optionally an after-treatment with H<sub>2</sub>O<sub>2</sub> can be applied.

The Denim material to be lightened is treated with the lightening liquid at a pH of about 4 at a temperature of, for example, 87°C.

Fono discloses a process for stripping dyes from dyed textile materials wherein a stripping liquid

is used consisting of an aqueous solution of a combination of

- a) a hydroxyalkan sulfinic acid salt as reducing agent (Fono, col. 2, lines 67-68),
- b) ammonium cations and
- c) sulfite anions.

Additional auxiliary agents can be applied.

The textile material to be stripped is treated in this stripping liquid at a pH of about 9 at a temperature of, for example, 190°F (~ 87°C) for about 30 minutes.

In order to show the differences between the processes of Fono and of the present invention and particularly the differences between the results obtained when applying the two processes I have the following comparison experiments performed by my assistant under my personal guidance and supervision:

Three 10 g samples were cut from a desized and stonewashed Denim cotton material whose warp threads had been dyed with 3 % (calculated on the weight of the thread material) of indigo.

A) The first sample was treated in accordance with Fono's stripping process (in analogy to Example 18, which is concerned with stripping a vat dyeing) as follows:

Preparation of the stripping liquid: A beaker was filled with 195 ml of water and 0.2 g ammonium sulfate and 0.2 sodium sulfite were added and heated to 87°C (190° F). The temperature was maintained at 87°C and 0.02 g of Primasol NF, a wetting and deaeration agent sold by BASF Aktiengesellschaft (ammonium salts of C<sub>13</sub>-C<sub>15</sub>-alkanol- phosphoric acid esters), and 6.67 g of a 30 % by weight aqueous solution (~ 2 g 100%) of sodium hydroxymethane sulfinic acid (commercial product marketed by BASF Aktiengesellschaft under the trade name <sup>TM</sup>Rongalit C liquid was used) and 0.2 g Peregall P, a leveling agent of BASF Aktiengesellschaft (oligomeric amide) were added.

Treatment of the sample: The first 10 gram sample of Denim fabric was immersed in the stripping liquid and treated therein under steady slight movement at 87 °C for 30 minutes. Then the sample was removed, rinsed with hot water containing 0.05% soap, finally with cold water and dried.

B) The second sample was treated in accordance with the lightening process of the present application as follows:

Preparation of the lightening liquid: A beaker was filled with 198 ml of water and heated to 87°C. 0.02 g of Primasol NF, a wetting and deaeration agent sold by BASF Aktiengesellschaft (ammonium salts of C<sub>13</sub>-C<sub>15</sub>-alkanol- phosphoric acid esters), and 0.2 g sodium hydroxymethane sulfinate and 0.2 g Peregal P, a leveling agent of BASF Aktiengesellschaft (oligomeric amide) and 4.17g of a 48 % by weight aqueous solution (~2 g 100%) of an equimolar mixture of N(CH<sub>2</sub>-SO<sub>2</sub>)<sub>3</sub>Na<sub>3</sub> and N(CH<sub>2</sub>-SO<sub>3</sub>)<sub>3</sub>Na<sub>3</sub> (commercial product marketed by BASF Aktiengesellschaft under the trade name <sup>TM</sup>Cyclanon ECO was used) were added.

Treatment of the sample: The second 10 gram sample of Denim fabric was immersed in the lightening liquid and treated therein under steady slight movement at 87 °C for 30 minutes. Then the sample was removed, rinsed with hot water containing 0.05% soap, finally with cold water and dried.

C) The third 10 g sample of the Denim fabric remained untreated.

Composition of the showing:

Each of the three samples was divided into three equal cuts and a cut of the untreated material a cut of the material treated according to Fono and a cut treated according to the present application were fixed side by side to a card board upon which had been written the corresponding recipes.

The same way two more identic specimen of the showing were produced.

Discussion of the demonstrated results:

It is evident that the difference between the processes of Fono and of the present application is not only a difference in degree but in kind. Whereas both processes result in a lightening of the dyeing, in the process of Fono the typical jeans character of the lightened textile material is completely lost, in the process of the present invention, however, the jeans character is perfectly retained and even increased. The showing clearly demonstrates that Fono's process, though it may be applied for stripping indigo dyeings, is absolutely unsuitable for the lightening of Denim material, because the desired jeans effect is lost.

Such differences in the outcome of the treatments according to the processes of Fono and of the present application could not be expected. Even now, in view of the facts, there is no verifiable explanation found for this surprising effect.

In addition to Fono's Patent the Examiner has cited WO 98/03725 to Beckman concerning a process for the reductive post-cleaning of freshly dyed polyester textile material, whereby various compounds summarized under the formulas I and II on pages 3 and 4 of WO 98/03725, namely hydroxy alkane sulfinates, alkoxyalkane sulfinates, dialkylether-disulfinates, aminoalkane sulfinates, hydroxy alkane sulfonates, alkoxyalkane sulfonates, dialkylether-disulfonates, aminoalkane sulfonates, or dithionites can be used as reducing agent.

In paper no. 4, point 12, the Examiner says that the lightening process of the present application were anticipated or obvious over Beckmann's post cleaning method.

One cannot agree to the Examiner's point of view.

It is true, that in Beckmann's process *inter alia* aminoalkane sulfinates can be employed but they are employed for a completely different purpose.

Whereas the process of the present application is designed to lighten cellulose fibers dyed with vat dyes, particularly with indigo, Beckmann's process is designed to remove an adsorptive layer of molecular dispersed dyestuff from the surface of polyester fiber.

The fundamental differences between these two processes are as follows:

Native cellulose fibers, e.g. cotton fibers, consist of a complex structure of cellulose fibrils forming several layers surrounding a central cavity [1; 2].

Vat dyes are pigments, i.e. colored, finely divided solids, absolutely insoluble in water.

Vat dyeing of cellulose comprises reductive conversion of the water insoluble pigment form of the dyestuff into its readily water soluble „leuko“ form, absorption of the leuco dyestuff by the cellulose fibrils and oxydative re-conversion of the leuco dyestuff into the completely insoluble pigment form, the pigment particles now being „trapped“ within the cellulose fiber. [3; 4]

**The present process is to attack the pigment particles trapped and bound inside the cellulose fiber in order to remove certain portions thereof out of the fiber without allowing the removed dyestuff to enter into the white weft threads of the Denim material.**

Turning now to Beckmann's post-cleaning process for dyed polyester:

Polyester fiber, a man made fiber, consists of a multitude of endless filaments lying side by side or being slightly wound to a rope. The single filament consists of a compact mass of polyester [5].

Dyeing of the polyester filament is carried out with disperse dyestuffs, finely divided, colored solids of very low solubility in water but much higher solubility in the polyester material.

Due to this difference in solubility the dyestuff tends, in accordance with Nernst's law of distribution [6], to transit from the aqueous phase into the polyester phase.

Such transition occurs during dyeing according to the following mechanism, which fundamentally differs from the vat dyeing mechanism:

At the dyeing temperature small amounts of disperse dyestuff dissolve in the aqueous dyeing liquor. From this solution single molecules of the dyestuff are adsorbed to the surface of the polyester filament forming thereon a thin adsorption layer of high dyestuff concentration. From this layer dyestuff molecules diffuse, in accordance with Fick's first law of diffusion, into the interior of the filaments where they remain in molecular distribution, thus forming a „solid solution“ [6].

Dyestuff molecules diffusing from the adsorption layer into the fiber are immediately replaced by dyestuff molecules from the aqueous liquor so that the dyestuff concentration in the adsorption layer is kept constant.

Consequently, at the end of dyeing there remains necessarily the thin adsorption layer of single dyestuff molecules on the filament surface.

**Beckman's post-cleaning process** is to remove this thin adsorption layer of molecular disperse dyestuff from the filament surface. For this purpose Beckman suggests to employ the various compounds summarized under the formulas I and II on pages 3 and 4 of WO 98/03725, comprising, together with at least 9 other types of compounds mentioned above, aminoalkane sulfinates.

No reason is seen for an artisan to assume, that a certain selection from these series of compounds, namely aminoalkane sulfinates could be excellently suited for the quite different purpose of partially removing vat dye pigment out of cellulose warp fibers of denim fabric without allowing them to stain the white weft fibers.

Further, and more precisely, the Examiner sets out in paper no. 7, page 4, lines 8 to 18, that an artisan being aware of Fono's stripping process wherein hydroxyalkane sulfinate is used together with ammonium kations could come to the conclusion – particularly in view of Beckmanns post cleaning process – that stripping should be possible also with aminoalkane sulfinate.

Again one cannot agree to this line of argumentation because of two reasons:

1) In view of the result of Fono's process, in respect of the total loss of the typical jeans character, an artisan whose problem was to lighten Denim, particularly jeans textile material, would not

have taken into consideration Fono's process as a starting point for the development of a process solving his problem.

2) Whereas hydroxyalkan sulfinate does react with ammonia or organic amines to give aminoalkan sulfonates it does not react with ammonium kation. This fact is well known to someone skilled in the art and, therefore, an artisan would not assume that Fono's process could be performed using aminoalkane sulfonate in place of hydroxyalkane sulfinate + ammonium kation.

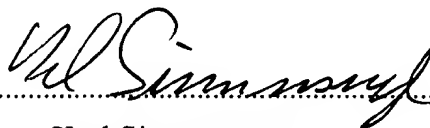
But even if an artisan had erroneously assumed that using a combination of hydroxyalkane sulfinic acid + ammonium kation would be equivalent to the use of aminoalkane sulfinic acid, then – in view of the unacceptable result of Fono's process – he would have come to the conclusion that treatment of Denim material with aminoalkane sulfinate likewise would destroy the desired jeans look.

Moreover, with respect to the quite different fields of stripping and post-cleaning technologies, no reason is seen for someone skilled in the art, before the present invention was disclosed, to consider Fono's process „in view“ of Beckmanns teaching or *vice versa*.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Ludwigshafen,

this 3<sup>rd</sup> day of November 2003



Karl Siemensmeyer

**U.S. Patent Application Serial No. 09/644,220**

Declaration of Karl Siemensmeyer, of November 03, 2003.

List of cited Literature.

- 1) Ullmann's Encyclopedia of Industrial Chemistry, 2<sup>nd</sup> Ed., Vol. 6, page 399-400, Chapter „Physical Properties“, particularly page 399, the last three lines and page 400 Figs. 3 and 4.
- 2) Ullmann's Encyclopedia of Industrial Chemistry, 6<sup>th</sup> Ed., Vol. 6, page 598 –599, Chapter „1.1.2. Supramolecular Structure (Texture)“, referring to Fig. 3 on page 599 and Fig. 5 on page 600.
- 3) Kirk-Othmer, Encyclopedia of Chemical Technology, 2<sup>nd</sup> Ed. Vol. 7, page 554, Chapter „Vat Dyes“, particularly the 2<sup>nd</sup> paragraph.
- 4) Kirk-Othmer, Encyclopedia of Chemical Technology, 4<sup>th</sup> Ed., Vol. 8, page 674, paragraph „Vat Dyes“.
- 5) Alfons Hofer, Textil und Modelexikon, 7<sup>th</sup> Ed., Vol 2, page 694, left col., raster electron microphotograph of polyester fibers. (Text below the picture: „Modification of polyester fibers by different shape of cross section. 1.7 dtex fibers, left hand side with normal round cross section, right hand side with trilobale cross section, the latter varying gloss and hand.“)
- 6) Ullmann's Encyclopedia of Industrial Chemistry, 6<sup>th</sup> Ed., Vol. 36, page 218, right col., Chapter 7.7.1, first and third paragraph; page 219, left col., first and second paragraph.

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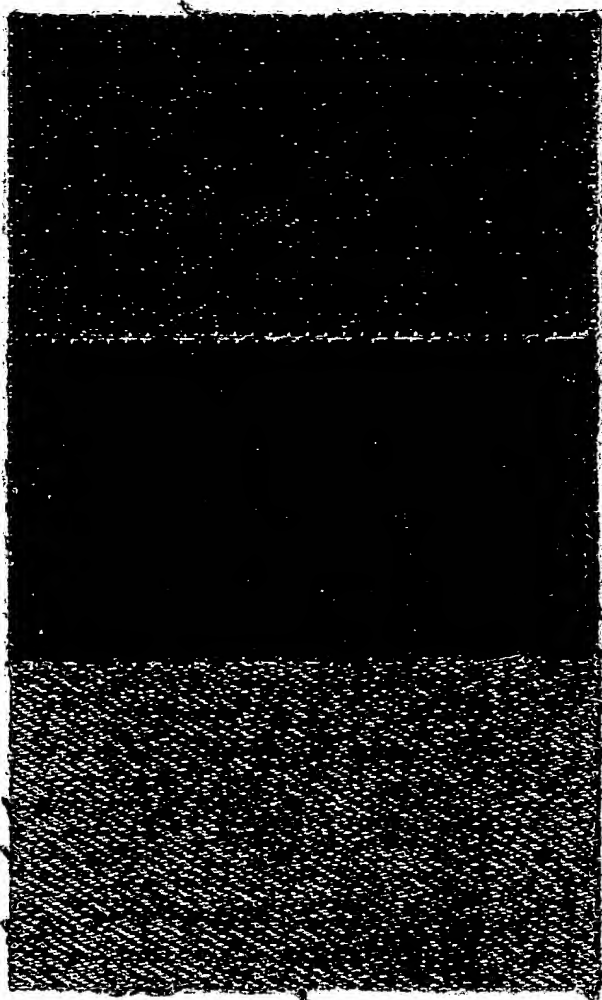
Declaration of Karl Siemensmeyer, of November 03, 2003.

Comparison between the processes of US-A-4,227,881 to Fono and  
of the present Application.

General Conditions:

Textile material: Cellulose, DENIM, warp indigo-dyed, desized, stone washed.  
Liquid ratio: 1 : 20  
Treatment: 30 min. at 87°C.  
Aftersoaping: 80°C using Uniperol 0 microperl

Sample



Treatment and recipe of liquor

Original DENIM textile material,  
not treated

According to Fono:

1.0 g/l levelling agent  
0.1 g/l wetting agent  
1.0 g/l di-ammonium sulfate  
1.0 g/l di-ammonium sulfite  
10 g/l HO-CH<sub>2</sub>-SO<sub>2</sub>Na

According to the present Application:

1.0 g/l levelling agent  
0.1 g/l wetting agent  
10 g/l N-(-CH<sub>2</sub>-SO<sub>3</sub>)<sub>1.5</sub>(CH<sub>2</sub>-SO<sub>2</sub>)<sub>1.5</sub>  
acetic acid, 60 % by weight, to adjust  
liquor to pH 4.0